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COMMITTEE OF EXPERTS ON THE TRANSPORT
OF DANGEROUS GOODS

REPORT OF THE COMMITTEE OF EXPERTS ON ITS SIXTEENTH SESSION

(3-12 December 1990)

Addendum 3

Annex 4: Adopted text and amendments to chapters 3, 4, 5, 6 and 7 of the Recommendations on the Transport of Dangerous Goods (Sixth revised edition) (ST/SG/AC.10/Rev.6).

GE.90-24603/5165a

CHAPTER 3

(1) Delete the following Special Provisions:

SP 41, SP 150, SP 151, SP 154, SP 211

(2) Amend Special Provision 63 to read:

63: "The division of Class 2 and the subsidiary risks depend on the nature of the contents of the aerosol or small receptacle. Division 2.1 applies if the contents include more than 45% by mass, or more than 250 g, of flammable components. Flammable components are gases which are flammable in air at normal pressure or substances or preparations in liquid form which have a flash point less than or equal to 100° C."

Amend existing Special Provisions as follows:

(a) Add the following sentence to the end of Special Provisions 44, 102, 112 and 185:

"Substances not meeting the criteria of Packing Group I, II or III are considered non-dangerous provided they do not meet the definition of any other class or division."

(b) In Special Provisions 129 and 192, insert the words "or non-dangerous" immediately preceding the words "according to grouping criteria".

(c) Add the following sentence to the end of Special Provision 184:

"Substances not meeting the criteria of Packing Groups II or III are considered non-dangerous provided they do not meet the definition of any other class or division."

(d) Replace the text of Special Provision 194 with:

"The control and emergency temperatures, if any, and the generic entry number for each of the currently assigned self-reactive substances are given in table 14.1."

(e) 168: "Asbestos which is immersed or fixed in a natural or artificial binder (such as cement, plastics, asphalt, resins or mineral ore) in such a way that no escape of hazardous quantities of respirable asbestos fibres can occur during transport is considered non-dangerous for transport. Manufactured articles containing asbestos and not meeting this requirement are nevertheless considered non-dangerous for transport when packed so that no escape of hazardous quantities of respirable asbestos fibres can occur during transport."

(f) 178: for "... with the approval of the competent authority."

read "... with the approval of the competent authority of the country of origin."

(g) 198: "Nitrocellulose solutions containing not more than 20% nitrocellulose may be transported as paint or printing ink as applicable. See UN 1210, 1263 and 3066."

(3) Insert new entries after Special Provision 203 as follows:

204 Articles containing smoke-producing substance(s) corrosive according to the criteria for Class 8 should be labelled with a "CORROSIVE" subsidiary-risk label.

205 This entry should not be used for PENTACHLOROPHENOL, UN 3155.

206 This entry is not intended to include ammonium permanganate, the transport of which should be prohibited except with special authorization granted by the competent authorities.

207 These beads may be made from polystyrene, poly (methyl methacrylate) or other polymeric material.

208 The commercial grade of calcium nitrate fertilizer, when consisting mainly of a double salt (calcium nitrate and ammonium nitrate) containing not more than 10% ammonium nitrate and at least 12% water of crystallization, is considered non-dangerous.

209 The gas should be at a pressure corresponding to ambient atmospheric pressure at the time the containment system is closed and this should not exceed 105 kPa absolute. The gas should be contained in hermetically sealed glass or metal inner packagings and with a maximum net quantity per package of 5 litres or, in the case of a toxic gas, a maximum net quantity per package of 1 litre.

210 Toxins from plant, animal or bacterial sources which contain infectious substances, or are contained in them, should be classified as Division 6.2.

212 Packing Group I or II according to grouping criteria.

213 Self-reactive substances of type F may be transported in intermediate bulk containers (IBCs) provided the requirements of 14.2.2.9 and Chapter 16 are satisfied.

214 For certain self-reactive substances of types B or C, a smaller packaging than that allowed by packing methods OP5A (or OP5B) or OP6A (or OP6B) respectively should be used (see 14.2.2.7.4 and table 14.1).

215 When the SADT is higher than 75° C, the technically pure substance and formulations derived from it should not be regarded as self-reactive substances.

The requirements of special provision 181 should be applied to formulations showing a violent effect in laboratory tests involving heating under confinement.

The packing method should be one of the following:

(i) a fibre drum, which may be lined, of maximum contents 50 kg;

(ii) an inner packaging of a single plastics bag in a fibreboard box, of maximum contents 50 kg; or

(iii) inner packagings of plastics bottles, jars, bags or boxes, of maximum contents 5 kg each, within an outer packaging of fibreboard box or drum of maximum contents 25 kg.

216 Mixtures of non-dangerous solids and flammable liquids may be transported under this entry without first applying the classification criteria of Division 4.1, provided there is no free liquid visible at the time the substance is loaded or at the time the packaging or transport unit is closed. Each packaging or transport unit should be leakproof.

217 Mixtures of non-dangerous solids and poisonous liquids may be transported under this entry without first applying the classification criteria of Division 6.1, provided there is no free liquid visible at the time the substance is loaded or at the time the packaging or transport unit is closed. Each packaging or transport unit should be leakproof. This entry should not be used for solids containing a Packing Group I liquid.

218 Mixtures of non-dangerous solids and corrosive liquids may be transported under this entry without first applying the classification criteria of Class 8, provided there is no free liquid visible at the time the substance is loaded or at the time the packaging or transport unit is closed. Each packaging or transport unit should be leakproof.

219 Substances transported under this entry should be packaged in accordance with 6.13. Genetically modified micro-organisms which are infectious should be transported as UN 2814 or UN 2900.

220 The technical name of the flammable liquid component only of this solution or mixture should be shown in parenthesis immediately following the Proper Shipping Name.

221 Substances included under this entry should not be of Packing Group I and should have a maximum net quantity per package of 5 litres or 5 kg.

222 Where the term "water-reactive" is used to describe a substance in these Recommendations, it means a substance which in contact with water emits flammable gas.

223 If the chemical or physical properties of a substance covered by this description are such that when tested it does not meet the established defining criteria for the class or division listed in column (b1), or any other class or division, it is considered non-dangerous.

CHAPTER 4

(a) In paragraph 4.3.1 delete the second sentence.

(b) In paragraph 4.4.1:

Replace the third sentence by two new sentences to read:

"Assessment of the compatibility group is usually made without test data except for Compatibility Groups N and S for which testing is necessary. In the case of Compatibility Group S the tests may be waived by the competent authority if classification by analogy is possible using test results for a comparable article."

(d) In paragraph 4.4.4 add at the end the following sentence:

"Compatibility Groups N and S should be used if justified by the results of tests."

(e) In paragraph 4.8 (glossary):

Delete from the descriptions of the terms "Cartridges for weapons" and "CARTRIDGES, SMALL ARMS" the word "military".

In the description of "Charges, propelling" print the name in capital letters, delete the words "in a cannon or" and add at the end "or for reducing the drag of projectiles". In the French text replace "réduire" by "modifier".

In the description of "POWDER, SMOKELESS" add at the end the phrase "or CHARGES, PROPELLING FOR CANNON". Last words "Charges, propelling" should be printed in capital letters.

In the description of "Propellants add at the end "or for reducing the drag of projectiles".

Insert a new entry to read:

"CHARGES, PROPELLING FOR CANNON

Articles consisting of a propellant charge in any physical form, with or without a casing, for use in a cannon."

(f) Table 4.3:

Delete the entries 0273, 0274 and 0416.

Add the entry "0491" to the term "Charges, propelling".

Add the entries 0492 and 0493 to the term "signals" (English version only).

Add the entry "0494" to the term "Jet perforating guns, oil well".

READEX FICHE

CHAPTER 5

In 5.4 amend the United Kingdom entry to:

"United Kingdom (British Standards Institution, Linford Wood,
Milton Keynes, MK14 6LE
British Standard BS 2000 Part 34
British Standard BS 2000 Part 170"

CHAPTER 6

(a) Amend paragraph 6.6 to read:

"6.6 Classification of pesticides

6.6.1 All active pesticide substances and their preparations for which the LC_{50} and/or LD_{50} values are known and which are classified in Division 6.1 should be classified under appropriate Packing Groups in accordance with the criteria given in paragraph 6.4. Substances and preparations which are characterized by subsidiary risks should be classified according to the precedence of hazard table with the assignment of appropriate Packing Group.

6.6.2 If the LC_{50} and/or LD_{50} values of the active pesticide substance or preparation are not known but the active substance is named in table 6.1, such substance or preparations containing this substance in concentrations mentioned in table 6.1 and which are characterized as having no subsidiary risks should be classified in Division 6.1 and assigned to the Packing Group as shown in table 6.1. Preparations containing the active substance in concentrations below the minimum stated in the Packing Group III columns of table 6.1 are considered non-dangerous. Active substances and preparations which are named in table 6.1, and which are characterized by subsidiary risks should be classified using the precedence of hazard table.

6.6.3 If preparations of pesticides cannot be classified according to paragraphs 6.6.1 and 6.6.2 and the LD_{50} value of their active substance is known, the LD_{50} value of such preparations can be obtained from the following formula:

$$LD_{50} \text{ value of preparation} = \frac{LD_{50} \text{ value of active substance} \times 100}{\text{percentage of active substance by mass}}$$

6.6.4 A classification according to paragraphs 6.6.2 and 6.6.3 should not be carried out when a preparation contains additives which affect the overall toxic hazard, or when a preparation contains several active substances. In such cases the classification should be based on the LC_{50} and/or LD_{50} values of the preparation as a whole, determined according to the criteria in the table in 6.4.1. If the LC_{50} and/or LD_{50} values are not known, the preparation should be classified under Packing Group I."

(b) Amend subparagraph 6.9 (a) to read:

"(a) 'Infectious substances' are those substances containing viable micro-organisms, including a bacterium, virus, rickettsia, parasite, fungus, or a recombinant, hybrid or mutant, that are known or reasonably believed to cause disease in animals or humans."

(c) Amend the text of the Note at the end of paragraph 6.9 (a) to read:

"Note: Toxins from plant, animal or bacterial sources which do not contain any infectious substances or organisms or which are not contained in them should be considered for transport as UN 3172."

(d) Add at the end of subparagraph 6.9 (b) the following Note:

"Note: Some licensed vaccines may present a biohazard only in certain parts of the world. In that case competent authorities may require these vaccines to comply with the requirements for infectious substances or may impose other restrictions."

(e) In paragraph 6.9 insert a new subparagraph (d) to read:

"(d) For purposes of these recommendations biological products and diagnostic specimens are divided into the following groups:

(1) those known or thought likely to contain infectious substances. For example, diagnostic specimens to undergo confirmatory testing should be considered to fall within this group

(2) those where a relatively low probability exists that infectious substances are present. For example, diagnostic specimens being transported to undergo routine screening tests or for the purpose of initial diagnosis should be considered to fall within this group.

(3) those known not to contain infectious substances."

(f) Delete the text of paragraph 6.10 and replace it by two new paragraphs:

"6.10.1 Biological products known to contain, or thought likely to contain, any infectious substances should meet all the requirements for infectious substances. Biological products referred to in paragraph 6.9 (d) (2) should meet all the provisions for infectious substances except when the following conditions are met:

(a) the primary receptacle(s) contains (contain) not more than 50 ml;

(b) the outer packaging contains not more than 50 ml when fragile primary receptacle(s) is (are) used and 100 ml for other primary receptacle(s);

(c) the primary receptacle(s) is (are) leakproof; and

(d) the packaging is in accordance with paragraph 6.13.

6.10.2 Diagnostic specimens known to contain, or thought likely to contain, any infectious substances should meet all the requirements for infectious substances. Diagnostic specimens referred to in paragraph 6.9 (d) (2) should meet all the provisions for infectious substances except when the following conditions are met:

(a) the primary receptacle(s) contains (contain) not more than 100 ml;

(b) the outer packaging contains not more than 500 ml;

(c) the primary receptacle(s) is (are) leakproof; and

(d) the packaging is in accordance with paragraph 6.13."

(g) In paragraph 6.13.3 amend:

"the primary receptacle and the secondary packaging" to read:

"the primary receptacle or the secondary packaging".

(h) Modify the text after the first sentence in paragraph 6.14.3 to read:

"For outer packagings, the headings in the table relate to fibreboard or similar materials whose performance may be rapidly affected by moisture; plastics which may embrittle at low temperature; and other materials such as metal whose performance is not affected by moisture or temperature. Where a primary receptacle and a secondary packaging of an inner packaging are made of different materials, the material of the primary receptacle determines the appropriate test. In instances where a primary receptacle is made of two materials, the material most liable to damage should determine the appropriate test."

6.9 (a) Change the present "Note" to "Note 1".

Add "Note 2. For the purposes of these recommendations, genetically modified substances are divided into the following groups:

(a) genetically modified micro-organisms which meet the definition of an infectious substance given above should be classified in Division 6.2 and assigned UN number 2814 for 2900;

(b) animals which contain, or are contaminated with, genetically modified substances that meet the definition of an infectious substance should be transported in accordance with chapter 6 and assigned UN number 2814 or 2900;

(c) except when authorized for unconditional use by the Governments of the countries of origin, transit and destination, genetically modified micro-organisms which do not meet the definition of infectious substances and which are capable of altering animals, plants or microbiological substances in a way not normally the result of natural reproduction should be assigned UN number 3245;

(d) genetically modified organisms, which are known or suspected to be dangerous to humans, animals or the environment, should be transported according to relevant national regulations."

CHAPTER 7

In paragraph 7.1 amend the third sentence to read:

"The IAEA Regulations contain the following specific restriction:

Account shall be taken of the formation of other dangerous substances which may result from the reaction between the contents of a consignment and the atmosphere or water in the event of breaking of the containment system caused by an accident (see para. 208 of the IAEA Regulations)." (Note that clause (b) is thereby deleted).

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Addendum 4

Annex 5 - Adopted text and amendments to chapters 9, 10, 11, 12 and 13 of the Recommendations on the Transport of Dangerous Goods (Sixth revised edition) (ST/SG/AC.10/1/Rev.6)

CHAPTER 9

(a) Amend the last sentence of paragraph 9.1.5 to read:

"The packagings used for organic peroxides and self-reactive substances should comply with the requirements for the medium danger category (Packing Group II) mentioned in 9.1.3."

(b) Insert a new paragraph 9.1.9 to read as follows:

"Packagings used for solids which may become liquid at temperatures likely to be encountered during transport should also be capable of containing the substance in the liquid state."

(c) Insert in paragraph 9.3.12 immediately after clause (b) the following new sentence:

"The inner receptacle of composite packagings may be tested without the outer packaging provided the test results are not affected."

(d) Amend the beginning of 9.4.4 to read:

"The letters 'V' or 'W' may follow the packaging code. The letter 'V' signifies a special packaging, see 9.7.1.7. The letter 'W' signifies that the packaging, although of the same type ..."

(e) Paragraph 9.7.1.6, add at the end:

"In addition, provided an equivalent level of performance is maintained, the following variations in inner packagings are allowed without further testing of the package:

(a) Inner packagings of equivalent or smaller size may be used provided:

(i) The inner packagings are of similar design to the tested inner packagings (e.g. shape - round, rectangular, etc.);

(ii) The material of construction of the inner packagings (glass, plastics, metal, etc.) offers resistance to impact and stacking forces equal to or greater than that of the originally tested inner packaging;

(iii) The inner packagings have the same or smaller openings and the closure is of similar design (e.g. screw cap, friction lid, etc.);

(iv) Sufficient additional cushioning material is used to take up void spaces and to prevent significant movement of the inner packagings;

(v) Inner packagings are oriented within the outer packaging in the same manner as in the tested package;

(b) A lesser number of the tested inner packagings, or of the alternative types of inner packagings identified in (a) above, may be used provided sufficient cushioning is added to fill the void space(s) and to prevent significant movement of the inner packagings."

(f) Insert a new paragraph 9.7.1.7 to read:

"9.7.1.7 Inner packagings of any type for solids or liquids may be assembled and transported without testing in an outer packaging under the following conditions:

(a) The outer packaging should have been successfully tested in accordance with 9.7.3 with fragile (e.g. glass) inner packagings using the Packing Group I drop height.

(b) The total combined gross mass of inner packagings should not exceed one half the gross mass of inner packagings used for the drop test in (a) above.

(c) The thickness of cushioning material between inner packagings and between inner packagings and the outside of the packaging should not be reduced below the corresponding thicknesses in the originally tested packaging; and when a single inner packaging was used in the original test, the thicknesses of cushioning between inner packagings should not be less than the thickness of cushioning between the outside of the packaging and the inner packaging in the original test. When either fewer or smaller inner packagings are used (as compared to the inner packagings used in the drop test), sufficient additional cushioning material should be used to take up void spaces.

(d) The outer packaging should have passed successfully the stacking test in 9.7.6 while empty. The total mass of identical packages should be based on the combined mass of inner packagings used for the drop test in (a) above.

(e) Inner packagings containing liquids should be completely surrounded with a sufficient quantity of absorbent material to absorb the entire liquid contents of the inner packagings.

(f) When the outer packaging is intended to contain inner packagings for liquids and is not leakproof, or is intended to contain inner packagings for solids and is not siftproof, a means of containing any liquid or solid contents in the event of leakage should be provided in the form of a leakproof liner, plastics bag or other equally efficient means of containment.

(g) For air transport, packagings should comply with 9.3.4.1.

(h) Packagings should be marked in accordance with 9.5 as having been tested to Packing Group I performance for combination packagings. The marked gross mass in kilogrammes should be the sum of the mass of the outer packaging plus one half of the mass of the inner packaging(s) as used for the drop test referred to in (a) above."

(g) Renumber paragraphs 9.7.1.7 and 9.7.1.8 as 9.7.1.8 and 9.7.1.9.

(h) Amend paragraph 9.7.2.1 to read:

"9.7.2.1 Tests should be carried out on packagings prepared as for transport including, with respect to combination packagings, the inner packagings used. Inner or single receptacles of packagings should be filled to not less than 98% of their capacity for liquids or 95% for solids. For combination packagings where the inner packaging is designed to carry liquids and solids, separate testing is required for both liquids and solid contents. The substances or articles to be transported in the packagings may be replaced by other substances or articles except where this would invalidate the results of the tests. For solids, when another substance is used it should have the same physical characteristics (mass, grain size, etc.) as the substance to be carried. It is permissible to use additives, such as bags of lead shot, to achieve the requisite total package mass, so long as they are placed so that the test results are not affected."

(i) The existing text of 9.7.2.3 should be retained, with the addition of the following note:

"Note. Average values should fall within these limits. Short-term fluctuations and measurement limitations may cause individual measurements to vary by up to ±5% relative humidity without significant impairment of test reproducibility."

CHAPTER 10

(a) In table 10.1:

In E3, column 3 delete: "steel, removable head (1A2) with coating other than lead".

In E102, E106, E112 and E119, column 3 under the heading "Boxes" insert in the appropriate line the terms "plastics, solid (4H2)".

In E137, insert in column 3 after the heading "Boxes" a new first line "fibreboard (4G)". In column 4 add Ppr "56";

Also in column 3 after "reconstituted wood" add "plastics, solid (4H2)".

(b) In table 10.2, Particular Packing Requirement 54:

For to accumulate read to generate and/or accumulate.

Delete the word "inner".

Insert a new particular packing requirement to read:

"56. Fibreboard boxes (4G) should not be used as outer packaging for UN 0106 or UN 0107."

CHAPTER 11

(1) Add to 11.3.3.3 (g):

"If the formulation is not thermally stable or a diluent other than type A is used for desensitization, the formulation should be defined as ORGANIC PEROXIDE TYPE F."

(2) In 11.3.8.1 add "metal" before "packagings".

CHAPTER 12

(a) In paragraph 12.1.1, first sentence, delete "except air transport".

(b) In paragraph 12.2.2, second sentence, delete "of being carried by land or sea and".

(c) Amend paragraph 12.22.6 (a) to read:

"with a degree of filling, for liquids having a viscosity of less than 2,680 centistokes at 20° C, of more than 20% but less than 80%, unless the shells of tank-containers are divided by partitions or surge plates, into sections of not more than 7,500 litres capacity;".

(d) Table 12.1:

(1) Insert a new column (3) headed "Division". Renumber columns (3) to (8) as (4) to (9).

(2) Amend existing entries as follows:

"UN 1005	col.(3)	2.3	col.(4)	8			
1009		2.2					
1010		2.1					
1011		2.1					
1012		2.1					
1017		2.3		5.1			
1018		2.2					
1020		2.2					
1027		2.1					
1028		2.2					
1029		2.2				new col.(8)	1.23
1030		2.1					
1032		2.1					
1033		2.1					
1036		2.1					
1037		2.1					
1040		2.3		2.1			
1041	col.(3)	2.3	col.(4)	2.1			
1055		2.1					
1061		2.1					
1062		2.3					
1063		2.1					
1064		2.3		2.1			
1067		2.3		5.1			

UN 1075	2.1
1077	2.1
1079	2.3
1082	2.1
1083	2.1
1085	2.1
1086	2.1
1087	2.1
1581	2.3
1582	2.3
1858	2.2
1912	2.2
1958	2.2
1969	2.1
1973	2.2
1974	2.2
1976	2.2
1978	2.1
1983	2.2
2517	2.1
2602	2.2 "

(3) In table 12.1 add the following entries:

"(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
1021	1-Chloro-1,2,2,2-tetra-fluoroethane (R.124)	2.2	blank	10.30 9.80 7.87 6.81	Allowed	Normal	1.20	blank
1978	Propane mixtures	2.1		see 12.24.6	Allowed	Normal	see 12.40	blank
3159	1,1,1,2-Tetrafluoro-ethane (R134a)	2.2	blank	17.7 15.7 13.8 12.1	Allowed	Normal	1.03	blank
3220	Pentafluoroethane (R.125)	2.2	blank	34.34 30.73 27.44 24.42	Allowed	Normal	0.95	blank "

(e) In table 12.2 amend the following entries in the columns shown:

"UN 1198, column (3) 3/III, column (4) 8

UN 1210, column (2) Printing Ink, flammable

UN 1325, column (2) Flammable solid, organic, n.o.s.

UN 1428, column (3) 4.3/I

UN 1459, column (3) 5.1/184

UN 1750, column (2) Chloroacetic acid solution
column (3) 6.1/II
column (4) 8
column (7) A/12.7.3

UN 1992, column (3) 3/129

UN 2257, column (3) 4.3/I

UN 2427, column (2) Potassium chlorate, aqueous solution

UN 2428, column (2) Sodium chlorate, aqueous solution

UN 2429, column (2) Calcium chlorate, aqueous solution

UN 2495, column (4) 6.1, 8

UN 2626, column (2) Chloric acid, aqueous solution with not more than 10% chloric acid

UN 2679, column (3) 8/184

UN 2965, column (3) 4.3/I
column (5) 4
column (7) N.A.
column (8) 12.9.3"

(f) Add the following new entries:

UN No.	(3)	(4)	(5)	(6)	(7)	(8)	(9)
"1599	6.1/III		2.65	12.5.2	A/12.7.2	N	12.22.2
1731	8/III		2.65	6 mm	A/12.7.2	N	12.22.2
1755	8/III		2.65	6 mm	A/12.7.3	N	12.22.2
1757	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
1761	8/III	6.1	2.65	12.5.2	A/12.7.2	N	12.22.2
1783	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
1787	8/III		2.65	6 mm	A/12.7.3	N	12.22.2
1788	8/III		2.65	6 mm	A/12.7.3	N	12.22.2
1789	8/III		2.65	6 mm	A/12.7.3	N	12.22.2
1814	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
1819	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
1824	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
2501	6.1/III		2.65	12.5.2	A/12.7.2	N	12.22.2
2564	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
2677	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
2681	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2
2817	8/III	6.1	2.65	12.5.2	A/12.7.3	N	12.22.2
2818	8/III	6.1	2.65	12.5.2	A/12.7.2	N	12.22.2
2821	6.1/III		2.65	12.5.2	A/12.7.2	N	12.22.2
2837	8/III		2.65	12.5.2	A/12.7.2	N	12.22.2"

(g) Delete UN 1454, 1455, 1462, 1474, 1475, 1489, 1502, 1506, 1508, 1751.

(h) Add the following entries:

(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)	(9)
"2207	Isocyanates, n.o.s. or Isocyanate solutions, n.o.s., boiling-point not less than 300° C (9)	6.1/III	-	2.65	12.5.2	A/12.7.3	N	12.22.2
2478	Isocyanates, n.o.s. or Isocyanate solutions, n.o.s., flash-point less than 23° C (9)	3/II	6.1	4	12.5.2	N.A.	N	12.22.3
3176	Flammable solid, organic, molten, n.o.s.[7]	4.1/184		2.65	12.5.2	N.A.	N	12.22.5
3210	Chlorates, inorganic, aqueous solutions, n.o.s.	5.1/II		2.65	12.5.2	A/12.7.3	N	12.22.2
3211	Perchlorates, inorganic, aqueous solutions, n.o.s.	5.1/II		2.65	12.5.2	A/12.7.3	N	12.22.2
3213	Bromates, inorganic, aqueous solutions, n.o.s.	5.1/II		2.65	12.5.2	A/12.7.3	N	12.22.2
3214	Permanganates, inorganic, aqueous solutions, n.o.s.	5.1/II		2.65	12.5.2	A/12.7.3	N	12.22.2
3216	Persulphates, inorganic, aqueous solutions, n.o.s.	5.1/III		1.5	12.5.2	A/12.7.3	N	12.22.2
3218	Nitrates, inorganic, aqueous solutions, n.o.s.	5.1/184		2.65	12.5.2	A/12.7.3	N	12.22.2
3219	Nitrites, inorganic, aqueous solutions, n.o.s.	5.1/184		2.65	12.5.2	A/12.7.3	N	12.22.2
3250	Cloroacetic acid, molten	6.1/	8	2.65	12.5.2	N.A.	N	12.22.5"

CHAPTER 13

(a) Replace table 13.2 with the following:

"Table 13.2: LABELS FOR CLASS 2 GASES WITH SUBSIDIARY RISK(S)

Division	Subsidiary risk(s) shown in Chapter 2	Primary risk label (with Class number 2 in lower corner)	Subsidiary risk label(s)
2.1	None	2.1	None
2.2	None	2.2	None
	5.1	2.2	5.1
2.3	None	2.3	None
	2.1	2.3	2.1
	5.1	2.3	5.1
	5.1, 8	2.3	5.1, 8
	8	2.3	8
	2.1, 8	2.3	2.1, 8

,"

(b) In paragraph 13.3.1 (b) amend "non-flammable, compressed gases" to read "non-flammable, non-toxic gases" and amend "St. Andrew's Cross" to "An 'X'".

(c) In paragraph 13.3.2 CHANGE "a good" to "an item of dangerous goods".

(d) Paragraph 13.3.3 from third sentence delete "except of Class 2" and "or the letter 'E'".

(e) Delete table 13.3.

(f) Amend paragraph 13.3.5 to read:

"Labels identifying primary risks should conform to models Nos. 1 to 9 illustrated in 13.5.1. Labels identifying subsidiary risks should display only the appropriate symbol and should conform to models Nos. 01 to 08 illustrated in 13.5.2."

(g) Amend paragraph 13.3.6 to read:

"Three separate lebels have been provided for Class 2, one for flammable gases of division 2.1 (red), one for non-flammable, non-toxic gases of division 2.2 (green) and one for toxic gases of division 2.3 (white). When the list of dangerous goods indicates that a Class 2 gas possesses

single or multiple subsidiary risks, labels should be used in accordance with table 13.2. In each case, the primary risk label shown in column 2 of that table should conform to 13.5.1 (models Nos. 2.1, 2.2 or 2.3)."

(h) Replace the last sentence of 13.4.3 with the following:

"Where a package is required to bear an 'EXPLOSIVE' subsidiary risk label, that label should conform to 13.5.2 (model No. 01)."

(i) Amend 13.4.4 to read:

"In the case of primary risk labels for Class 5, the division number of the substance should be shown in the bottom corner of the label. For all other primary risk labels, the class number of the substance or article should be shown in the bottom corner of the label. Specimens of the primary risk labels for each class are given in 13.5.1 (models Nos. 1 to 9)."

(j) Insert new paragraph 13.4.9 to read as follows:

"13.4.9 Gas cylinders for Class 2 may, on account of their shape, orientation and securing mechanisms for transport, bear labels representative of those specified in this section, which have been reduced in size, as appropriate, for display on the non-cylindrical part (shoulder) of such cylinders."

(k) Replace the current 13.5 with a new 13.5 as follows:

13.5 Specimen labels

13.5.1 Specimen primary risk labels

CLASS 1

(No.1)
Divisions 1.1, 1.2 and 1.3

Explosive substances or articles
Symbol (exploding bomb): black; Background: orange; figure "1" in bottom corner.

* Place for division and compatibility group

(No.1.4)
Division 1.4

(No.1.5)
Division 1.5

(No.1.6)
Division 1.6

Background: orange; Figures: black; Numerals should be about 30 mm in height and be about 5 mm thick (for a label measuring 100 mm x 100 mm); figure "1" in bottom corner.

** Place for compatibility group

CLASS 2

(No.2.1)
Division 2.1

Flammable gases
Symbol (flame): black or white; Background: red; figure "2" in bottom corner.

(No.2.2)
Division 2.2

Non-flammable, non-taxic gases
Symbol (gas cylinder): black or white; Background: green; figure "2" in bottom corner.

(No.2.3)
Division 2.3

Toxic gases
Symbol (skull and crossbones) black; Background: white; figure "2" in bottom corner.

CLASS 3

(No.3)

Flammable liquids
Symbol (flame): black or white; Background: red; figure "3" in bottom corner.

CLASS 4

(No.4.1)
Division 4.1

Flammable solids
Symbol (flame): black;
Background: white with seven vertical red stripes;
Figure "4" in bottom corner.

(No.4.2)
Division 4.2

Substances liable to spontaneous combustion
Symbol (flame): black;
Background: upper half white; lower half red; figure "4" in bottom corner.

(No.4.3)
Division 4.3

Substances which in contact with water emit flammable gas.
Symbol (flame): black or white; Background: blue; figure "4" in bottom corner.

CLASS 5

(No.5.1)
Division 5.1

Oxidizing substances
Symbol (flame over circle): black; Background: yellow; figures "5.1" in bottom corner.

(No.5.2)
Division 5.2

Organic peroxides
Symbol (flame over circle): black; Background: yellow; figures "5.2" in bottom corner.

CLASS 6

(No.6.1)
Division 6.1

Poisonous (toxic) substances
Packing Groups: I and II
Symbol (skull and crossbones): black; Background: white; figure "6" in bottom corner.

(No.6.1A)
Division 6.1

Poisonous (toxic) substances
Packing Group III
The bottom half of the label may bear "Harmful" and the inscription: "Stow away from foodstuffs"
Symbol (An "X" over an ear of wheat) and Inscription: black; Background: white; figure "6" in bottom corner.

(No.6.2)
Division 6.2

Infectious substances
The bottom half of the label may bear: "Infectious Substance" and the inscription: "In the case of damage or leakage immediately notify Public Health authority"; Symbol (three crescents superimposed on a circle) and Inscription: black; Background: white; figure "6" in bottom corner.

CLASS 7

(No.7A) (No.7B) No.7C)

Radioactive material

7A Category I - White; Symbol (trefoil): black; Background: white; Text (mandatory) black in bottom half of label: "Radioactive"; "Contents ...", "Activity ...". One red vertical stripe must follow the word "Radioactive"; figure "7" in bottom corner.

7B Category II - Yellow; Symbol (threfoil): black; Background: upper half yellow with white border, bottom half white; Text (mandatory) black in bottom half of label: "Radioactive"; "Contents ..."; "Activity ..."; in a black outlined box - "Transport Index". Two red vertical stripes must follow the word "Radioactive"; figure "7" in bottom corner.

7C Category III - Yellow; Symbol (trefoil): black; Background: upper half yellow with white border, bottom half white; Text (mandatory) black in bottom half of label; "Radioactive"; "Contents ..."; "Activity ..."; in a black outlined box - "Transport Index". Three red vertical stripes must follow the word "Radioactive"; figure "7" in bottom corner.

CLASS 8

(No.8)

Corrosive substances
Symbol (liquids, spilling from two glass vessels and attacking a hand and a metal): black; upper half white, lower half black with white border; figure "8" in white in bottom corner.

CLASS 9

(No.9)

Miscellaneous dangerous substances
Symbol (seven vertical stripes in upper half): black;
Background: white; small figure "9" underlined in bottom corner.

13.5.2 Specimen subsidiary risk labels

(No.01) (No.03) (No.04.1)

(No.04.2) (No.04.3) (No.05)

(No.06.1 (No.08)
(Packing Groups I and II))

13.5.3 DISPLAY OF UN NUMBERS ON PLACARDS

* location of class or division number
** location of UN number

Figure 13.1

Figure 13.2

Figure 13.3

PLACARD FOR RADIOACTIVE MATERIALS OF CLASS 7

(No.7D)

Symbol (trefoil): black; Background: top half yellow with white border, bottom half white. The bottom half should show the appropriate UN number (see para.13.7.5) and/or the word "RADIOACTIVE"; and the figure "7" in the bottom corner.

Figure 13.4

DANGEROUS GOODS TRANSPORT DOCUMENT

In the box "Marks & number" etc., insert the words:

"PACKING GROUP;" after "UN NUMBER;"

(l) In paragraph 13.6.1, clause (b) delete the third sentence.

Amend clause (c) to read:

"(c) The UN No. and, where assigned, the Packing Group for the substance or article;"

(m) In paragraph 13.6.1.4 replace "flammable solids" with "self-reactive and related substances".

(n) Insert a new paragraph 13.6.1.5 to read:

"13.6.1.5 When organic peroxides and self-reactive substances are transported under conditions where notification is required (for organic peroxides see 11.3.2.5, 11.3.12.2, 12.551 and 12.553; for self-reactive substances see 14.2.2.3.3 and 14.2.2.9.1), a statement to this effect should be included in the transport document. A copy of the statement of approval of the classification for non-listed organic peroxides and self-reactive substances should be attached to the transport document."

Insert a new paragraph 13.6.1.6 to read:

"13.6.1.6 When a sample of an organic peroxide (see 11.3.2.6) or a self-reactive substance (see 14.2.2.3.5) is transported, a statement to this effect should be included in the transport document."

(o) Amend paragraph 13.6.6 to read:

"... of the form shown in figure 13.4 ...".

(p) Amend paragraph 13.7.1.2, second sentence, to read: "... is otherwise as shown in figure 13.3 ...".

(q) Amend paragraph 13.7.5, to read:

"- against a white background in the lower half of the placard (see figures 13.1 and 13.3); or

- on an orange rectangular panel not less than 120 mm high and 300 mm wide, with a 10 mm black border, to be placed immediately adjacent to the placard (see figure 13.2)."

(r) In paragraph 13.8.4, amend the end of the last sentence but two to read: "... the technical name of the goods and the applicable packing group."

and amend the last two sentences to read:

"The technical name should be shown in parentheses immediately following the proper shipping name, unless a national law or international convention prohibits its disclosure if it is a controlled substance. The particular 'N.O.S.' or 'generic' entries for which this supplementary information is considered necessary are marked by an asterisk at the end of the proper shipping name shown in column (a2) of the list in chapter 2."

(s) In paragraph 13.8.5, amend the end of the penultimate sentence to read:

"... need to be shown, excluding controlled substances when their disclosure is prohibited by national law or international convention."

(t) In paragraph 13.8.5.1, delete the reference to UN No. 1954.

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COMMITTEE OF EXPERTS ON THE TRANSPORT
OF DANGEROUS GOODS

REPORT OF THE COMMITTEE OF EXPERTS ON ITS SIXTEENTH SESSION
(3-12 December 1990)

Addendum 5

Annex 6: TEXT and amendments to Chapter 14 of the Recommendations on the Transport of Dangerous Goods (Sixth revised edition) (ST/SG/AC.10/Rev.6)

SPECIAL RECOMMENDATIONS RELATING TO CLASS 4

14.1 General Notes

14.1.1 Attention is drawn to chapter 1, paragraph 1.21, which describes the three divisions of Class 4.

14.1.1.1 Division 4.1 comprises the following types of substances:

(a) flammable solids (see 14.2.1);

(b) self-reactive and related substances (see 14.2.2); and

(c) desensitized explosives (see 14.2.3);

14.1.1.2 Division 4.2 comprises:

(a) pyrophoric substances (see 14.3.1.1(a)); and

(b) self-heating substances (see 14.3.1.1(b)).

14.1.1.3 Division 4.3 comprises substances which in contact with water emit flammable gas (see 14.4).

14.1.2 Because of the different properties exhibited by dangerous goods within Divisions 4.1 and 4.2, it is impracticable to establish a single criterion for classification in either of these divisions. Tests and criteria for assignment to the three divisions of Class 4 are addressed in 14.5.

14.1.3 Text unchanged

14.2 Division 4.1 - Flammable solids, self-reactive and related substances, and desensitized explosives

14.2.1 Division 4.1 - (a) Flammable solids

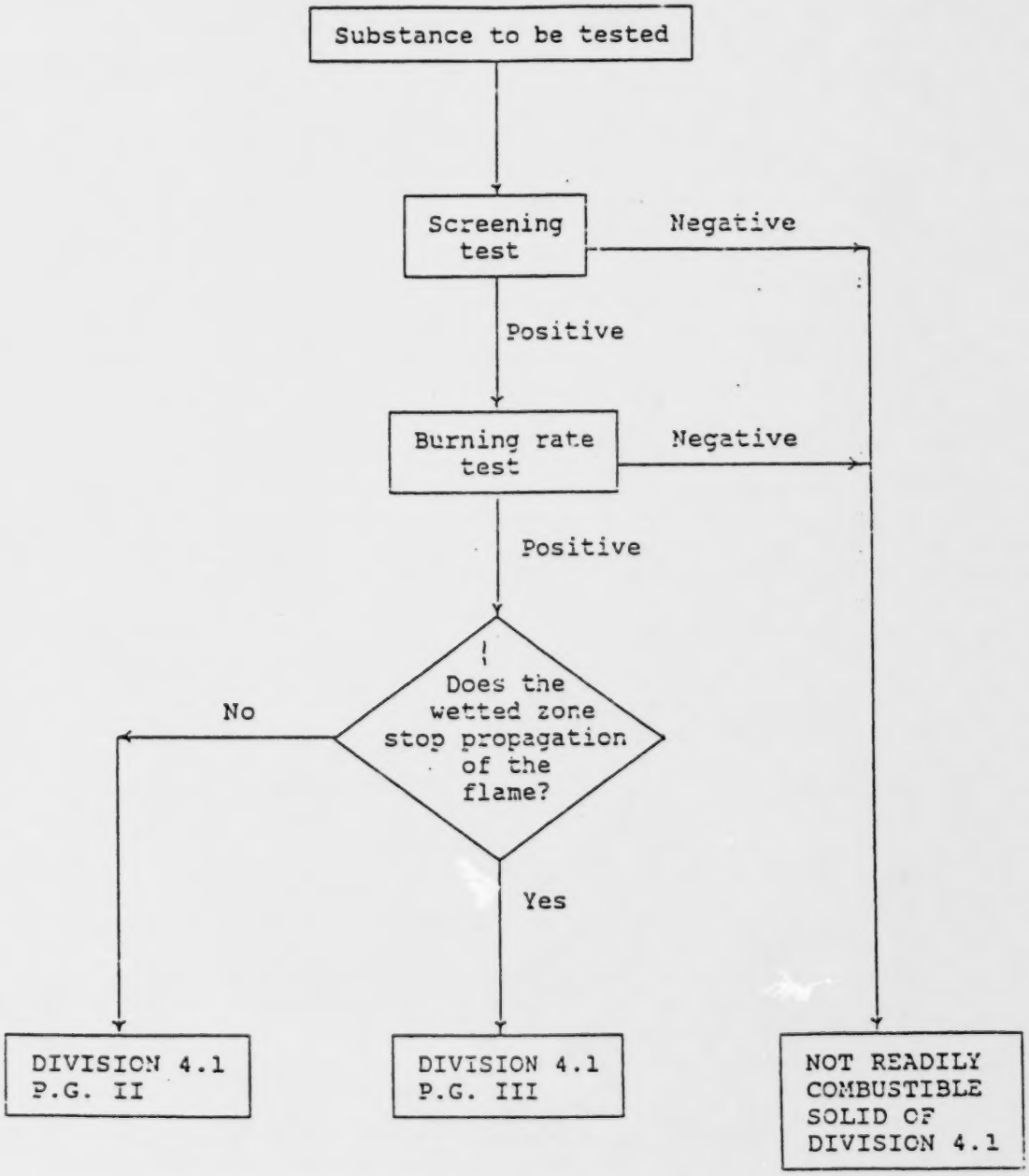
14.2.1.1 Properties

14.2.1.1.1 Flammable solids are readily combustible solids and solids which may cause fire through friction. Readily combustible solids are powdered, granular, or pasty substances which are dangerous if they can be easily ignited by brief contact with an ignition source, such as a burning match, and if the flame spreads rapidly. The danger may come not only from the fire but also from toxic combustion products. Metal powders are especially dangerous because of the difficulty of extinguishing a fire since normal extinguishing agents such as carbon dioxide or water can increase the hazard.

14.2.1.2 Classification of flammable solids

14.2.1.2.1 Flammable solids should be classified in Division 4.1 in accordance with the test methods and criteria described in 14.5.2 and the procedure indicated in the flow chart, Figure 14.1.

Figure 14.1: FLOW CHART FOR ASSIGNING READILY COMBUSTIBLE SOLIDS, EXCEPT METAL POWDERS, TO DIVISION 4.1



14.2.1.2.2 Solids which may cause fire through friction should be classified in Division 4.1 by analogy with existing entries (e.g. matches) until definitive criteria are established.

14.2.1.3 Assignment of new flammable solids to Packing Groups

14.2.1.3.1 For readily combustible solids (other than metal powders) which are tested in accordance with the test methods and criteria in 14.5.2, Packing Group II should be assigned if the burning time is less than 45s and the flame passes the wetted zone. Packing Group II should be assigned to powders of metal or metal alloys if the zone of reaction spreads over the whole length of the sample in five minutes or less.

14.2.1.3.2 For readily combustible solids (other than metal powders), Packing Group III should be assigned if the burning time is less than 45s and the wetted zone stops the flame propagation for at least four minutes. Packing Group III should be assigned to metal powders if the reaction spreads over the whole length of the sample in more than five minutes but not more than ten minutes.

14.2.1.3.3 For solids which may cause fire through friction, the Packing Group should be assigned by analogy with existing entries or in accordance with any appropriate special provision.

14.2.1.4 Assignment of existing entries to Packing Groups

14.2.1.4.1 Readily combustible solids and solids which may cause fire through friction are flammable solids with a wide range of properties. Some of these substances have been assigned to Packing Group II on the basis of experience and judgement of their characteristics, such entries in chapter 2 are:

(a) Wetted pyrophoric powders:

1326 HAFNIUM POWDER, WETTED etc.;
1352 TITANIUM POWDER, WETTED etc.;
1358 ZIRCONIUM POWDER, WETTED etc.

These powders of Division 4.1 are wetted with sufficient water to suppress pyrophoric properties.

(b) Other substances, or articles:

1309 ALUMINIUM POWDER COATED - an ignitable element, see also 14.2.1.4.2 (d);
1323 FERROCERIUM - lighter flints, emit sparks when struck;
1333 CERIUM, slabs, ingots or rods - slabs, ingots and rods show a tendency to ignite;
1339 PHOSPHORUS HEPTASULPHIDE, free from yellow and white phosphorus;
1341 PHOSPHORUS SESQUISULPHIDE, etc.;
1343 PHOSPHORUS TRISULPHIDE, etc. - these sulphides may ignite through friction to give off flammable and toxic fumes;

1347 ZIRCONIUM HYDRIDE - is stable in air and water, the hydrogen content is 1.7% to 2.1%; when ignited it burns with incandescence and mild explosions;
1868 DECABORANE - is stable indefinitely at room temperature but decomposes slowly to give off hydrogen at 300° C;
1871 TITANIUM HYDRIDE - dissociates to give off hydrogen above 288° C;
2623 FIRELIGHTERS, SOLID with flammable liquid - the flash-point of the impregnating liquid is < 23° C. See also 14.2.1.4.2 (f);
2989 LEAD PHOSPHITE DIBASIC - is readily ignited, sustaining combustion; see, however, Special Provision 184.

(c) Collective entries:

1325 FLAMMABLE SOLID, ORGANIC, N.O.S;
2925 FLAMMABLE SOLID, ORGANIC, [X2] CORROSIVE, N.O.S;
2926 FLAMMABLE SOLID, ORGANIC, [X2] POISONOUS, N.O.S;
3089 METAL POWDERS, FLAMMABLE, N.O.S;
3097 FLAMMABLE SOLID, OXIDIZING, N.O.S;
3175 SOLIDS CONTAINING FLAMMABLE LIQUID, N.O.S;
3176 FLAMMABLE SOLID, ORGANIC MOLTEN, N.O.S;
3178 FLAMMABLE SOLID, INORGANIC, N.O.S;
3179 FLAMMABLE SOLID, INORGANIC, POISONOUS, N.O.S;
3180 FLAMMABLE SOLID, INORGANIC, CORROSIVE, N.O.S;
3181 METAL SALTS OF ORGANIC COMPOUNDS, FLAMMABLE, N.O.S;
3182 METAL HYDRIDES, FLAMMABLE, N.O.S.

These entries should be used in accordance with 1.39.1; see, however, Special Provisions 184 and 192, as appropriate, and 14.2.1.4.2 (g).

14.2.1.4.2 Some readily combustible solids and solids which may cause fire through friction have been assigned to Packing Group III on the basis of experience and judgement of their characteristics. Such entries in chapter 2 are:

(a) Flammable solids:

UN Nos. 1313, 1314, 1318, 1324, 1327, 1328, 1330, 1353, 2000, 2001, 2538, 2687, 2714, 2715.

These substances have given a positive reaction in a burning rate test.

(b) Organic subliming solids:

1312 BORNEOL;
1334 NAPHTHALENE, CRUDE or NAPHTHALENE, REFINED;
2304 NAPHTHALENE, MOLTEN;
2717 CAMPHOR, synthetic.

These substances give variable results in a burning rate test as the rate of sublimation is affected by the ambient starting temperature and air flow.

(c) Organic polymers, depolymerizing at low temperatures:

1322 METALDEHYDE;
2213 PARAFORMALDEHYDE.

These substances may also give variable results in a burning rate test.

(d) Ignitable elements:

UN Nos. 1338, 1346, 1350, 1869, 2448, 2858, 2878.

These substances are known to be readily ignitable in practice and/or difficult to extinguish, but give variable results in a burning rate test. Uncharacteristic results with metal powders are caused by the method of production, leading to surface oxidation, which inhibits ignition; see also 14.2.1.4.1 (b).

(e) Matches:

1331 MATCHES, "STRIKE ANYWHERE";
1944 MATCHES, SAFETY etc.;
1945 MATCHES, WAX "VESTA";
2254 MATCHES, FUSEE.

These products ignite by friction, but some types require a specially prepared surface.

(f) Firelighters:

2623 FIRELIGHTERS, SOLID with flammable liquid.

The flash-point of the impregnating liquid is $\geq$ 23° C and $<$ 61° C; see also 14.2.1.4.1 (b).

(g) Collective entries:

1325 FLAMMABLE SOLID, ORGANIC, N.O.S;
2925 FLAMMABLE SOLID, ORGANIC, [X2] CORROSIVE, N.O.S;
2926 FLAMMABLE SOLID, ORGANIC, [X2] POISONOUS, N.O.S;
3089 METAL POWDERS, FLAMMABLE, N.O.S;
3097 FLAMMABLE SOLID, OXIDIZING, N.O.S;
3176 FLAMMABLE SOLID, ORGANIC MOLTEN, N.O.S;
3178 FLAMMABLE SOLID, INORGANIC, N.O.S;
3179 FLAMMABLE SOLID, INORGANIC, POISONOUS, N.O.S;
3180 FLAMMABLE SOLID, INORGANIC, CORROSIVE, N.O.S;
3181 METAL SALTS OF ORGANIC COMPOUNDS, FLAMMABLE, N.O.S;
3182 METAL HYDRIDES, FLAMMABLE, N.O.S.

These entries should be used in accordance with 1.39.1; see, however, Special Provisions 184 and 192, as appropriate, and 14.2.1.4.1 (c).

14.2.2 Division 4.1 - (b) Self-reactive and related substances

14.2.2.1 Definition

14.2.2.1.1 Self-reactive substances are substances liable to undergo (at normal or elevated temperatures) a strongly exothermic decomposition caused by excessively high transport temperatures. Substances should not be considered to be self-reactive substances of Division 4.1, if:

they are explosives according to the criteria of Class 1;

they are oxidizing substances according to the assignment procedure of Division 5.1 (see 11.2.1);

they are organic peroxides according to the criteria of Division 5.2;

their heat of decomposition is less than 300 J/g; or

their self-accelerating decomposition temperature is greater than 75° C.

Note: The heat of decomposition can be determined using any internationally recognised method e.g. Differential Scanning Calorimetry and adiabatic calorimetry.

14.2.2.2 Properties

14.2.2.2.1 The decomposition of self-reactive substances can be initiated by heat, contact with catalytic impurities (e.g. acids, heavy-metal compounds, bases), friction or impact. The rate of decomposition increases with temperature and varies with the substance. Decomposition, particularly if no ignition occurs, may result in the evolution of toxic gases or vapours. For certain self-reactive substances, the temperature should be controlled. Some self-reactive substances may decompose explosively, particularly if confined. This characteristic may be modified by the addition of diluents or by the use of appropriate packagings. Some self-reactive substances burn vigorously. Self-reactive substances are, for example, some compounds of the types listed below:

aliphatic azo compounds (-C-N=N-C-);

organic azides (-C-N_3);

diazonium salts (-$CN_2^+Z^-$);

N-nitroso compounds (-N-N=O); and

aromatic sulphohydrazides (-SO_2-NH-NH_2).

This list is not exhaustive and substances with other reactive groups and some mixtures of substances may have similar properties.

14.2.2.3 Classification

14.2.2.3.1 Self-reactive substances are classified into seven types according to the degree of danger. The principles to be applied to the classification of substances are set out in 14.2.2.4. The types of self-reactive substance range from type A, which should not be accepted for transport in the packaging in which it is tested, to type G, which is not subject to the provisions for self-reactive substances of Division 4.1. The classification of types B to F is directly related to the maximum quantity allowed in one packaging.

Related substances have been assigned to packing groups II or III. UN 2956 is such an entry.

14.2.2.3.2 Self-reactive substances listed in Table 14.1 have been assigned to generic entries in chapter 2 with UN numbers 3221 to 3240. The generic entries specify:

self-reactive substance type (B to F) (see 14.2.2.4.2);

physical state (liquid/solid) (see 14.2.2.7.4);

temperature control (when required) (see 14.2.2.5).

14.2.2.3.3 Classification of self-reactive substances not listed in table 14.1 and assignment to a generic entry should be made by the competent authority of the country of origin. A notification should be sent by the competent authority of the country of origin or the consignor to the competent authority of the country of destination, if so required by it. The notification should contain:

a statement of approval by the competent authority of the country of origin of the classifcation and conditions of transport; and

a report with the test results (see 14.2.2.4.3).

14.2.2.3.4 Activators, such as zinc compounds, may be added to some self-reactive substances to change their reactivity. Depending on both the type and the concentration of the activator, this may result in a decrease in thermal stability and a change in explosive properties. If either of these properties is altered, the new formulation should be assessed in accordance with the classification procedure.

14.2.2.3.5 Samples of self-reactive substances or formulations of self-reactive substances not listed in Table 14.1, for which a complete set of test results is not available and which are to be transported for further testing or evaluation, should be assigned to one of the appropriate entries for self-reactive substances type C provided the following conditions are met:

the available data indicates that the sample would be no more dangerous than self-reactive substances type B;

the sample is packaged in accordance with packing method OP2A or OP2B (see 11.3.9) and the quantity per transport unit is limited to 10 kg; and

the available data indicate that the control temperature, if any, is sufficiently low to prevent any dangerous decomposition and sufficiently high to prevent any dangerous phase separation.

In such cases, the notification procedure described in 14.2.2.3.3 is not required (see 13.6.1.6).

14.2.2.4 Principles for classification for self-reactive substances

14.2.2.4.1 A self-reactive substance should be regarded as possessing explosive properties when in laboratory testing the formulation is liable to detonate, to deflagrate rapidly or to show a violent effect when heated under confinement.

14.2.2.4.2 The following principles should be applied to the classification of self-reactive substances not listed in Table 14.1:

(a) Any substance which can detonate or deflagrate rapidly, as packaged for transport, should be prohibited from transport under the provisions for self-reactive substances of Division 4.1 in that packaging (defined as self-reactive substance type A, exit box A of Figure 14.2).

(b) Any substance possessing explosive properties and which, as packaged for transport, neither detonates nor deflagrates rapidly, but is liable to undergo a thermal explosion in that package, should also bear an "EXPLOSIVE" subsidiary risk label.
Such a substance may be packaged in amounts of up to 25 kg unless the maximum quantity has to be limited to a lower amount to preclude detonation or rapid deflagration in the package (defined as self-reactive substance type B, exit box B of Figure 14.2).

(c) Any substance possessing explosive properties may be transported without an "EXPLOSIVE" subsidiary risk label when the substance as packaged (maximum 50 kg) for transport cannot detonate or deflagrate rapidly or undergo a thermal explosion (defined as self-reactive substance type C, exit box C of Figure 14.2).

(d) Any substance which in laboratory testing:

detonates partially, does not deflagrate rapidly and shows no violent effect when heated under confinement; or

does not detonate at all, deflagrates slowly and shows no violent effect when heated under confinement; or

does not detonate or deflagrate at all and shows a medium effect when heated under confinement;

may be accepted for transport in packages of not more than 50 kg net mass (defined as self-reactive substance type D, exit box D of Figure 14.2).

(e) Any substance which, in laboratory testing, neither detonates nor deflagrates at all and shows low or no effect when heated under confinement may be accepted for transport in packages of not more than 400 kg/450 litres (defined as self-reactive substance type E, exit box E of Figure 14.2).

(f) Any substance which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows only a low or no effect when heated under confinement as well as low or no explosive power may be considered for transport in IBCs (defined as self-reactive substance type F, exit box F of Figure 14.2); for additional requirements see 14.2.2.9.

(g) Any substance which, in laboratory testing, neither detonates in the cavitated state nor deflagrates at all and shows no effect when heated under confinement nor any explosive power should be exempted from classification as a self-reactive substance of Division 4.1 provided that the formulation is thermally stable (self-accelerating decomposition temperature 60° C to 75° C for a 50 kg package) and any diluent meets the requirements of 14.2.2.6 (defined as self-reactive substance type G, exit box G of figure 14.2). If the formulation is not thermally stable or a diluent other than type A is used for desensitization, the formulation should be defined as SELF-REACTIVE LIQUID/SOLID TYPE F.

14.2.2.4.3 Paragraph 14.2.2.4.2 refers only to those properties of self-reactive substances which are decisive for their classification. A flow chart, presenting the classification principles in the form of a graphically arranged scheme of questions concerning the decisive properties together with the possible answers, is given in Figure 14.2. These properties should be determined experimentally using the test methods and criteria for organic peroxides, given in the current edition of the United Nations Recommendations, Tests and Criteria.

14.2.2.5 Temperature control requirements

Self-reactive substances should be subject to temperature control if their SADT is less than or equal to 55° C. Test methods for determining the SADT are given in the current edition of the Recommendations: Tests and Criteria. The test selected should be conducted in a manner which is representative, both in size and material, of the package to be transported. The recommendations for organic peroxides given in 11.3.5.1 to 11.3.5.3, concerning temperature control and derivation of control and emergency temperatures, should be applied analogously to self-reactive substances.

Figure 14.2: FLOW CHART FOR ASSIGNING SELF-REACTIVE SUBSTANCES TO DIVISION 4.1

Editorial Note
Secretariat to use ISO information exchange symbols when flow chart agreed by Committee
SELF-REACTIVE SUBSTANCE
Box 1
Does it propagate a detonation?
1.1 Yes
1.2 Partial
1.3 No
Box 2
Can it detonate as packaged for transport?
2.1 Yes
2.2 No
Exit A
NOT ACCEPTED FOR TRANSPORT AS A SELF-REACTIVE SUBSTANCE OF DIVISION 4.1 IN THAT PACKAGING
Box 4
Can it propagate a deflagration?
4.1 Yes, rapidly
4.2 Yes, slowly
4.3 No
Box 5
Does it deflagrate rapidly in package?
5.1 Yes
5.2 No
Box 6
What is the effect of heating it under defined confinement?
6.1 Violent
6.2 Medium
6.3 Low
6.4 No
Box 7
What is the effect of heating it under defined confinement?
7.1 Violent
7.2 Medium
7.3 Low
7.4 No
Box 12
Can it explode as packaged for transport?
12.1 Yes
12.2 No
Exit B
ACCEPTED FOR TRANSPORT IN PACKAGES OF NOT MORE THAN 25 KG NET MASS WITH "EXPLOSIVE" SUBSIDIARY RISK LABEL (see 14.2.2.4.2(b))
Exit C
ACCEPTED FOR TRANSPORT IN PACKAGES OF NOT MORE THAN 50 KG NET MASS (see 14.2.2.4.2(c))
Exit D
ACCEPTED FOR TRANSPORT IN PACKAGES OF NOT MORE THAN 50 KG NET MASS
Box 3
Can it propagate a deflagration?
3.1 Yes, rapidly
3.2 Yes, slowly
3.3 No
Box 7 bis
Is it to be considered for transport in IBCs or exemption?
Yes
No
Exit E
ACCEPTED FOR TRANSPORT IN PACKAGES OF NOT MORE THAN 400 KG / 450 LITRES
Box 8
What is it's explosive power?
8.1 Not low
8.2 Low
8.3 No
Box 9
Does the cavitated substance propagate a detonation?
9.1 Yes
9.2 Partial
9.3 No
Box 10
What is the effect of heating it under defined confinement?
10.1 Low
10.2 No
Exit F
MAY BE CONSIDERED FOR TRANSPORT IN IBCS (see 14.2.2.4.2(f))
Box 11
Does the cavitated substance propagate a detonation?
11.1 Yes
11.2 Partial
11.3 No
Exit G
SHOULD BE CONSIDERED FOR EXEMPTION (see 14.2.2.4.2(g))

Table 14.1: LIST OF CURRENTLY ASSIGNED SELF-REACTIVE SUBSTANCES

Note. The classification given in this table is based on the technically pure substance (except where a concentration of less than 100% is specified). For other concentrations, the substances may be classified differently following the procedures in 14.2.2.4 and 14.2.2.5.

SELF-REACTIVE SUBSTANCE	Concentration (%)	Packing method	Control temperature (° C)	Emergency temperature (° C)	UN Generic entry	Remarks
AZODICARBONAMIDE FORMULATION TYPE B	<100	OP5B			3232	(1)(2)
AZODICARBONAMIDE FORMULATION TYPE C	<100	OP6B			3234	(3)
AZODICARBONAMIDE FORMULATION TYPE D	<100	OP7B			3236	(4)
2,2' -AZODI(2,4-DIMETHYL-4-METHOXYVALERONITRILE)	100	OP7B	- 5	+ 5	3236	
2,2' -AZODI(2,4-DIMETHYLVALERONITRILE)	100	OP7B	+ 10	+ 15	3236	
2,2' -AZODI(ETHYL 2-METHYLPROPIONATE)	100	OP7A	+ 20	+ 25	3235	
1,1-AZODI(HEXAHYDROBEZONITRILE)	100	OP7B			3226	
2,2' -AZODI(ISOBUTYRONITRILE)	100	OP6B	+ 40	+ 45	3234	
2,2' -AZODI(2-METHYLBUTYRONITRILE)	100	OP7B	+ 35	+ 40	3236	
BENZENE-1,3-DISULPHOHYDRAZIDE, as a paste	52	OP7B			3226	
BENZENE SULPHOHYDRAZIDE	100	OP7B			3226	
4-(BENZYL(ETHYL)AMINO)-3-ETHOXYBENZENEDIAZONIUM ZINC CHLORIDE	100	OP7B	+ 40	+ 45	3236	
4-(BENZYL(METHYL)AMINO)-3-ETHOXYBENZENEDIAZONIUM ZINC CHLORIDE	100	OP7B	+ 40	+ 45	3236	

SELF-REACTIVE SUBSTANCE	Concentration (%)	Packing method	Control temperature (° C)	Emergency temperature (° C)	UN Generic entry	Remarks
3-CHLORO-4-DIETHYLAMINO-BENZENEDIAZONIUM ZINC CHLORIDE	100	OP7B			3226	
2-DIAZO-1-NAPHTHOL-4-SULPHOCHLORIDE	100	OP5B			3222	
2-DIAZO-1-NAPHTHOL-5-SULPHOCHLORIDE	100	OP5B			3222	
2,5-DIETHOXY-4-MORPHOLINO-BENZENEDIAZONIUM ZINC CHLORIDE	67-100	OP7B	+ 35	+ 40	3236	
2,5-DIETHOXY-4-MORPHOLINO-BENZENEDIAZONIUM ZINC CHLORIDE	66	OP7B	+ 40	+ 45	3236	
2,5-DIETHOXY-4-MORPHOLINO-BENZENEDIAZONIUM FLUOROBORATE	100	OP7B	+ 30	+ 35	3236	
2,5-DIETHOXY-4-(PHENYLSULPHONYL)BENZENEDIAZONIUM ZINC CHLORIDE	67	OP7B	+ 40	+ 45	3236	
2,5-DIMETHOXY-4-(4-METHYLPHENYLSULPHONYL)BENZENEDIAZONIUM ZINC CHLORIDE	79	OP7B	+ 40	+ 45	3236	
4-DIMETHYLAMINO-6-(2-DIMETHYLAMINOETHOXY) TOLUENE-2-DIAZONIUM ZINC CHLORIDE	100	OP7B	+ 40	+ 45	3236	
N,N'-DINITROSO-N,N'-DIMETHYL TEREPHTHALAMIDE, as a paste	72	OP6B			3224	
N,N'-DINITROSOPENTAMETHYLENE TETRAMINE, with diluent type A	82	OP7B			3224	
DIPHENYLOXIDE-4,4'-DISULPHOHYDRAZIDE	100	OP7B			3226	
4-DIPROPYLAMINOBENZENEDIAZONIUM ZINC CHLORIDE	100	OP7B			3226	

SELF-REACTIVE SUBSTANCE	Concentration (%)	Packing method	Control temperature (° C)	Emergency temperature (° C)	UN Generic entry	Remarks
2-(2-HYDROXYETHOXY)-1-PYRROLIDIN-1-YL)BENZENE DIAZONIUM ZINC CHLORIDE	100	OP7B	+ 45	+ 50	3236	
3-(2-HYDROXYETHOXY)-4-PYRROLIDIN-1-YL)BENZENE DIAZONIUM ZINC CHLORIDE	100	OP7B	+ 40	+ 45	3236	
4-METHLYBENZENESULPHONYL-HYDRAZIDE	100	OP7B	+ 40	+ 45	3236	
3-METHYL-4-(PYRROLIDIN-1-YL)BENZENEDIAZONIUM FLUOROBORATE	95	OP6B	+ 45	+ 50	3234	
N-FORMYL-2-(NITROMETHYLENE) -1,3-PERHYDROTHIAZINE	100	OP7B	+ 45	+ 50	3236	
2-(N,N-ETHOXYCARBONYL-PHENYLAMINO)-3-METHOXY-4-(N-METHYL-N-CYCLOHEXYL-AMINO)BENZENEDIAZONIUM ZINC CHLORIDE	63-92	OP7B	+ 40	+ 45	3236	
2-(N,N-ETHOXYCARBONYL-PHENYLAMINO)-3-METHOXY-4-(N-METHYL-N-CYCLOHEXYL-AMINO)BENZENEDIAZONIUM ZINC CHLORIDE	62	OP7B	+ 35	+ 40	3236	
2-(N,N-METHYLAMINOETHYL-CARBONYL)-4-(3,4-DIMETHYL-PHENYLSULPHONYLBENZENE-DIAZONIUM HYDROGEN SULPHATE	96	OP7B	+ 45	+ 50	3236	
SELF-REACTIVE LIQUID, SAMPLE		OP2A			3223	
SELF-REACTIVE LIQUID, SAMPLE, TEMPERATURE CONTROLLED		OP2A			3233	(5)
SELF-REACTIVE SOLID, SAMPLE		OP2B			3224	
SELF-REACTIVE SOLID, SAMPLE, TEMPERATURE CONTROLLED		OP2B			3234	(5)

SELF-REACTIVE SUBSTANCE	Concentration (%)	Packing method	Control temperature (° C)	Emergency temperature (° C)	UN Generic entry	Remarks
SODIUM 2-DIAZO-1-NAPHTHOL-4-SULPHONATE	100	OP7B			3226	
SODIUM 2-DIAZO-1-NAPHTHOL-5-SULPHONATE	100	OP7B			3226	
TETRAMINE PALLADIUM (II) NITRATE]	100	OP6B	+ 30	+ 35	3234	

Remarks

(1) Azodicarbonamide formulations which fulfil the criteria of 14.2.2.4.2(b). The control and emergency temperature should be determined by the procedure given in 11.3.5.1 to 11.3.5.3.

(2) "EXPLOSIVE" subsidiary risk label required.

(3) Azodicarbonamide formulations which fulfil the criteria of 14.2.2.4.2(c). The control and emergency temperature should be determined by the procedure given in 11.3.5.1 to 11.3.5.3.

(4) Azodicarbonamide formulations which fulfil the criteria of 14.2.2.4.2(d). The control and emergency temperature should be determined by the procedure given in 11.3.5.1 to 11.3.5.3.

(5) See 14.2.2.3.5.

14.2.2.6 Desensitization of self-reactive substances

14.2.2.6.1 In order to ensure safety during transport, self-reactive substances may be desensitized through the use of a diluent. If a diluent is used, the self-reactive substance should be tested with the diluent present in the concentration and form used in transport.

14.2.2.6.2 Diluents which may allow a self-reactive substance to concentrate to a dangerous extent in the event of leakage from a packaging should not be used.

14.2.2.6.3 The diluent should be compatible with the self-reactive substance. In this regard, compatible diluents are those solids or liquids which have no detrimental influence on the thermal stability and hazard type of the self-reactive substance.

14.2.2.6.4 Liquid diluents in liquid formulations requiring temperature control should have a boiling point of at least 60° C and a flash point not less than 5° C. The boiling point of the liquid should be at least 50° C higher than the control temperature of the self-reactive substance.

14.2.2.7 Packaging requirements for self-reactive substances

14.2.2.7.1 Packagings should satisfy the requirements of chapter 9 and should be so constructed that none of the materials in contact with the contents will catalyse or otherwise dangerously affect the properties of their contents. For combination packagings, cushioning materials should not be readily combustible and should not cause decomposition of the self-reactive substance if leakage occurs.

14.2.2.7.2 To avoid unnecessary confinement, metal packagings meeting the test criteria of packing group I should not be used. Self-reactive substances should be assigned to Packaging Group II (medium danger).

14.2.2.7.3 The packaging of a self-reactive substance required to bear an "EXPLOSIVE" subsidiary risk label should comply with 10.1.1 and 10.1.3.

14.2.2.7.4 The packing methods for organic peroxides in 11.3.9 should be used for self-reactive substances. Viscous liquids should be treated as solids if the criteria in 1.10 are met. The packing methods appropriate for the individual currently assigned self-reactive substances are listed in table 14.1. A packing method corresponding to a smaller package size (i.e. with a lower OP number) may be used but a packing method corresponding to a larger package size (i.e. with a higher OP number) should not be used.

14.2.2.7.5 For new self-reactive substances or new formulations of currently assigned self-reactive substances, the procedure in 11.3.9.3 for organic peroxide types B to F should be used to assign the appropriate packing method for self-reactive substance types B to F.

14.2.2.8 Transport under temperature control

14.2.2.8.1 The recommendations in 11.3.10 for the transport of organic peroxides under temperature control should be applied analogously to the transport of self-reactive substances.

14.2.2.9 Transport of self-reactive substances in IBCs

14.2.2.9.1 Self-reactive substances of type F may be transported in IBCs under conditions laid down by the competent authority of the country of origin when, on the basis of testing, the competent authority is satisfied that such transport may be safely conducted. The tests should include those necessary:

to prove that the self-reactive substance complies with the principles for classification given in 14.2.2.4.2(f);

to prove the compatibility of all materials normally in contact with the substance during the transport;

to determine the control and emergency temperatures, if required, for transport of the substance in the IBC concerned as derived from the SADT;

to design, when applicable, emergency-relief devices; and

to determine if any special requirements are necessary.

A notification, including the test results and the approved conditions of transport, should be sent to the competent authority of the country of destination by the competent authority of the country of origin or the consignor. The notification should contain:

a statement of approval by the competent authority of the country of origin of the classification and conditions of transport; and

a report with the test results.

14.2.2.9.2 To prevent explosive rupture of metal IBCs or composite IBCs with complete metal casing, the emergency-relief devices should be designed to vent all the decomposition products and vapours evolved during a period of not less than one hour of fire engulfment (heat load 110 kW/m^2) or self-accelerating decomposition.

14.2.2.10 Transport of packages in transport units

14.2.2.10.1 Where a number of packages are assembled in a transport unit, the total quantity of self-reactive substances, the type and number of packages and the stacking arrangement should not create an explosion hazard.

14.3 Division 4.2 - Substances liable to spontaneous combustion

14.3.1 Properties

14.3.1.1 Self-heating of substances, leading to spontaneous combustion, is caused by reaction of the substance with oxygen (in the air) and the heat developed not being conducted away rapidly enough to the surroundings. Spontaneous combustion occurs when the rate of heat production exceeds the rate of heat loss and the auto-ignition temperature is reached. Two types of substances can be distinguished with spontaneous combustion properties:

(a) Substances, including mixtures and solutions (liquid or solid), which even in small quantities ignite within five minutes of coming in contact with air. These substances are the most liable to spontaneous combustion and are called pyrophoric substances.

(b) Other substances which in contact with air without energy supply are liable to self-heating. These substances will ignite only when in large amounts (kilograms) and after long periods of time (hours or days) and are called self-heating substances.

14.3.2 Assignment to Division 4.2

14.3.2.1 Pyrophoric solids should be classified in Division 4.2 in accordance with the test method and criterion given in 14.5.3 and pyrophoric liquids by the test methods and criteria in 14.5.4.

14.3.2.2 Self-heating substances should be assigned to Division 4.2 in accordance with the test method and criteria in 14.5.5.

14.3.3 Assignment of Packing Groups

14.3.3.1 Packing Group I should be assigned to all pyrophoric solids and liquids.

14.3.3.2 Packing Group II should be assigned to self-heating substances which give positive results when tested with the 25 mm cube sample.

14.3.3.3 Packing Group III should be assigned to self-heating substances which give positive results when tested with the 100 mm^3 sample but which give a negative result with a 25 mm cube sample.

14.4 Division 4.3 - Substances which in contact with water emit flammable gases

14.4.1 Properties

14.4.1.1 Certain substances in contact with water may emit flammable gases that can form explosive mixtures with air. Such mixtures are easily ignited by all ordinary sources of ignition, for example naked lights, sparking handtools or unprotected light bulbs. The resulting blast wave and flames may endanger people and the environment. The test method in 14.5.6 should be used to determine whether the reaction of a substance with water leads to the development of a dangerous amount of gases which may be flammable. It should not be applied to pyrophoric substances.

14.4.2 Assignment to Division 4.3

14.4.2.1 Substances which in contact with water emit flammable gases should be assigned to Division 4.3 in accordance with the tests and criteria given in 14.5.6.

14.4.3 Assignment of Packing Groups

14.4.3.1 Packing Group I should be assigned to any substance which reacts vigorously with water at ambient temperatures and demonstrates generally a tendency for the gas produced to ignite spontaneously, or which reacts readily with water at ambient temperatures such that the rate of evolution of flammable gas is equal to or greater than 10 litres per kilogram of substance over any one minute.

14.4.3.2 Packing Group II should be assigned to any substance which reacts readily with water at ambient temperatures such that the maximum rate of evolution of flammable gas is equal to or greater than 20 litres per kilogram of substance per hour, and which does not meet the criteria for Packing Group I.

14.4.3.3 Packing Group III should be assigned to any substance which reacts slowly with water at ambient temperatures such that the maximum rate of evolution of flammable gas is greater than 1 litre per kilogram of substance per hour, and which does not meet the criteria for Packing Groups I or II.

14.5 Test methods and criteria for substances of Class 4

14.5.1 General

14.5.1.1 Test methods and criteria are given for the following types of substances of Class 4:

(a) flammable solids (Division 4.1);

(b) pyrophoric solids (Division 4.2);

(c) pyrophoric liquids (Division 4.2);

(d) self-heating substances (Division 4.2); and

(e) substances which in contact with water emit flammable gases (Division 4.3).

14.5.1.2 The test methods and criteria for organic peroxides (UN Recommendations: Tests and Criteria, Part III) should be applied to self-reactive substances requiring temperature control of Division 4.1.

14.5.2 Test methods for flammable solids

14.5.2.1 Preliminary screening test

(a) The substance in its commercial form, should be formed into an unbroken strip or powder train about 250 mm long by 20 mm wide by 10 mm high on a cool, impervious, low heat-conducting base plate.

(b) A hot flame (minimum temperature 1,000° C) from a gas burner (minimum diameter 5 mm) should be applied to one end of the powder train until the powder ignites or for a maximum of 2 minutes (5 minutes for powders of metals or metal alloys). It should be noted whether combustion propagates along 200 mm of the train within the 2 minute test period (or 20 minutes for metal powders).

(c) If the substance does not ignite and propagate combustion either by burning with flame or smouldering along 200 mm of the powder train within the 2 minute (or 20 minute) test period, then the substance should not be classified as a flammable solid and no further testing is required.

(d) If the substance propagates burning of a 200 mm length of the powder train in less than 2 minutes or less than 20 minutes for metal powders, the full test programme in 14.5.2.2 should be carried out.

14.5.2.2 Burning rate test

14.5.2.2.1 Principle of the method

In order to differentiate between any substance that can be ignited and those which burn rapidly or whose burning behaviour is particularly dangerous, only substances whose burning rate exceeds a certain limiting value should be classified in Division 4.1. A burning time of less than 45 s measured over a length of 100 mm according to the procedure in 14.5.2.2.2 should be the

criterion. An attempt should be made to ignite the substance under the conditions defined in 14.5.2.2.2 and the burning time measured. The pile is wetted beyond the zone over which the burning rate is measured and the effect on flame propagation is noted.

14.5.2.2.2 Procedure

(a) The powdered or granular substance, in its commercial form, should be loosely filled into a mould 250 mm long with a triangular cross-section of inner height 10 mm and width 20 mm. On both sides of the mould, in the longitudinal direction, two metal sheets are mounted as lateral limitations which extend 2 mm beyond the upper edge of the triangular cross-section (Figure 14.3). The mould is then dropped three times from a height of 20 mm on to a solid surface. The lateral limitations are then removed and the impervious, non-combustible, low heat-conducting plate is placed on top of the mould, the apparatus inverted and the mould removed. Pasty substances are spread on a non-combustible surface in the form of a rope 250 mm in length with a cross-section of about 100 mm^2. Any suitable ignition source such as a small flame or a hot wire of minimum temperature 1,000° C is used to ignite the pile at one end. In the case of a moisture sensitive substance, the test should be carried out as quickly as possible, after its removal from the container.

(b) The pile should be arranged across the draught in a fume cupboard. The air speed should be sufficient to prevent fumes escaping into the laboratory and should not be varied during the test. A draught screen may be erected around the apparatus.

(c) One ml of a wetting solution */ should be added to the pile 30-40 mm beyond the 100 mm timing zone. Apply the wetting solution to the ridge drop by drop, ensuring the whole cross-section of the pile is wetted without loss of liquid from the sides. The liquid should be applied over the shortest possible length of the pile consistent with avoiding loss from the sides. This part of the test is not applicable to metal powders.

(d) One end of the pile should be ignited. When the pile has burned a distance of 80 mm, measure the rate of burning over the next 100 mm. Note whether or not the wetted zone stops propagation of the flame. The test should be performed six times using a clean cool plate each time, unless a positive result is observed earlier.

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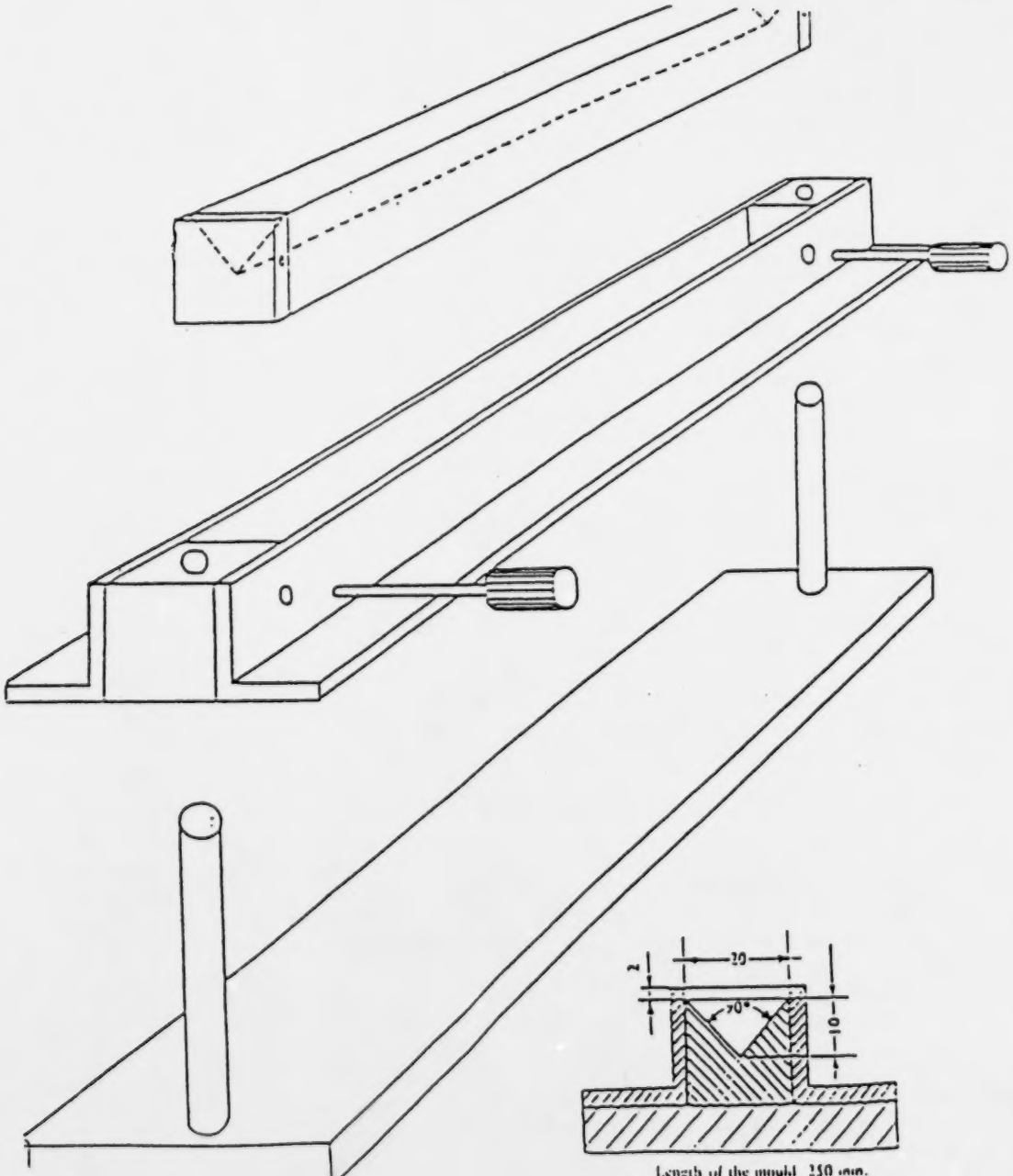
*/ With many substances, water rolls off the sides of the pile, so the addition of wetting agents may be necessary. Wetting agents used should be free from combustible diluents and the total active matter in the wetting solution should not exceed 1%. This liquid may be added to a hollow up to 3 mm deep and 5 mm in diameter in the top of the pile.

Figure I4.3: MOULD AND ACCESSORIES FOR THE PREPARATION OF THE PILE FOR THE BURNING RATE TEST



14.5.2.3 Criteria for classification

Powdered, granular or pasty substances should be classified in Division 4.1 when the time of burning of one or more of the test runs, in accordance with the test method described in 14.5.2.2, is less than 45 s or the rate of burning is more than 2.2 mm/s. Powders of metals or metal alloys should be classified when they can be ignited and the reaction spreads over the whole length of the sample in 10 minutes or less.

14.5.3 Test method for pyrophoric solids

14.5.3.1 Principle of the method and procedure

One to two ml of the powdery substance to be tested should be poured from about 1 m height onto a non-combustible surface and it is observed whether the substance ignites during dropping or within five minutes of settling. This procedure should be performed six times unless a positive result is obtained earlier.

14.5.3.2 Criterion for classification

If the sample ignites in one of the tests, the substance should be considered pyrophoric and should be classified in Division 4.2.

14.5.4 Test methods for pyrophoric liquids

14.5.4.1 Principle of the method

Liquid substances should be tested in two stages; the first determines if the substance ignites when added to an inert carrier and exposed to air, the second should be performed if a negative result is obtained in Part 1. The second part determines if the substance chars or ignites a filter paper.

14.5.4.2 Procedure

(a) Part 1 - A porcelain cup of about 100 mm diameter should be filled with diatomaceous earth or silica gel at room temperature to a height of about 5 mm. Approximately 5 ml of the liquid to be tested should be poured into the prepared porcelain cup and it is observed if the substance ignites within five minutes. This procedure should be performed six times unless a positive result is obtained earlier.

(b) Part 2 - A 0.5 ml test sample should be delivered from a syringe to an indented dry No. 3 Whatman filter paper. The test should be conducted at 25 ± 2° C and a relative humidity of 50 ± 5%. Observations are made to see if ignition or charring occurs on the filter paper within five minutes after the liquid to be tested is introduced. This procedure should be performed three times using fresh filter paper each time unless a positive result is obtained earlier.

14.5.4.3 Criteria for classification

If the liquid ignites in Part 1 of the test, or if it ignites or chars the filter paper in Part 2 of the test, it should be considered to be pyrophoric and should be classified in Division 4.2.

14.5.5 Test method for self-heating substances

14.5.5.1 Principle of the method

Samples in 25 mm and 100 mm cubes should be kept at a constant temperature for 24 hours and observations made on whether the temperature of the sample exceeds 200° C. (The test method is a modified version of the Bowes-Cameron cage test which is a self-heating test method for carbon).

14.5.5.2 Procedure

(a) A hot air circulating type of oven with an inner volume of more than 9 litres and capable of controlling the internal temperature at 140 ± 2° C should be used.

(b) Cubic sample containers of 25 mm and 100 mm side, made of stainless-steel net with a mesh opening of 0.053 mm, with their top surface open, should be used. Each container is housed in a cubic container cover made from a stainless-steel net with a mesh opening of 0.595 mm and slightly larger than the sample container, so that the container fits in this cover. In order to avoid the effect of air circulation, another stainless-steel cage, made from a net with a mesh opening of 0.595 mm and 150 x 150 x 250 mm in size, should be further installed to house the cover.

(c) Chromel-Alumel thermocouples of 0.3 mm diameter should be used for temperature measurement. One is placed in the centre of the sample and another between the sample container and the oven wall. The temperatures should be measured continuously.

(d) The sample, powder or granular, in its commercial form, should be filled to the brim of the sample container and the container tapped several times. If the sample settles, more is added. If the sample is heaped it should be levelled to the brim. The container is housed in the cover and hung at the centre of the oven.

(e) The oven temperature should be raised to 140° C and kept there for 24 hours. The temperature of the sample should be recorded. The first test should be conducted with a 100 mm cube sample. Observations are made to determine if spontaneous ignition occurs or if the temperature of the sample exceeds 200° C. If negative results are obtained no further test is necessary. If positive results are obtained a second test should be conducted with a 25 mm cube sample to determine the data for packing group assignment.

14.5.5.3 Criteria for classification

A substance should be classified in Division 4.2 if in the first test using a 100 mm cube sample, spontaneous ignition occurs or the temperature of the sample exceeds 200° C during the 24 hour testing time. This criterion is based on the self-heating temperature of charcoal, which is 50° C for a cubic volume of 27 m^3 and 140° C for a 1 litre sample. Substances with self-ignition temperatures higher than 50° C for 27 m^3 should not be classified in Division 4.2.

14.5.6 Test methods for substances which in contact with water emit flammable gases

14.5.6.1 Principle of the method

The substance should be tested in its commercial form at ambient temperature (20° C) by bringing it into contact with water. If spontaneous ignition of the gas occurs at any step, no further testing is necessary.

14.5.6.2 Procedure

14.5.6.2.1 A small quantity (approximately 2 mm diameter) of the test substance should be placed in a trough of distilled water at 20° C. It is noted (i) whether any gas is evolved and (ii) if spontaneous ignition of the gas occurs.

14.5.6.2.2 A small quantity of the test substance (approximately 2 mm diameter) should be placed on the centre of a filter paper which is floated flat on the surface of distilled water at 20° C in a suitable vessel, e.g. a 100 mm diameter evaporating dish. The filter paper is to keep the substance in one place, under which condition the likelihood of spontaneous ignition of any gas is greatest. It should be noted (i) whether any gas is evolved and (ii) if spontaneous ignition of the gas occurs.

14.5.6.2.3 The test substance should be made into a pile approximately 20 mm high and 30 mm diameter with a hollow in the top. A few drops of water are added to the hollow. It should be noted whether (i) any gas is evolved and (ii) if spontaneous ignition occurs.

14.5.6.2.4 For solid substances, the package should be inspected for any particles of < 500 um diameter. If that powder constitutes more than 1% (mass) of the total, or if the substance is friable, then the whole of the sample should be ground to a powder before testing to allow for a reduction in particle size during handling and transport. Otherwise, as for liquids, the substance should be tested in its commercial state. The test should be performed at ambient temperature (20° C) and atmospheric pressure, and performed three times.

14.5.6.2.5 Water is put into the dropping funnel and enough of the substance (up to a maximum mass of 25 g) to produce between 100 ml and 250 ml of gas is weighed and placed in a conical flask. The tap of the dropping funnel is opened to let the water into the conical flask and a stop watch is started. The volume of gas evolved is measured by any suitable means. The time taken for all the gas to be evolved is noted and where possible, intermediate readings are taken. The rate of evolution of gas is calculated over seven hours at one hour intervals. If the rate of evolution is erratic or is increasing after seven hours, the measuring time should be extended to a maximum time of five days. The five-day test may be stopped if the rate of evolution becomes steady or continually decreases and sufficient data has been established to assign a packing group to the substance or to determine that the substance should not be classified in Division 4.3. If the chemical identity of the gas is unknown, the gas should be tested for flammability.

14.5.6.3 Criteria for classification

A substance should be classified in Division 4.3 if:

(a) spontaneous ignition takes place in any step of the test procedure, or

(b) there is an evolution of a flammable gas at a rate greater than 1 litre per kilogram of the substance per hour.

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REPORT OF THE COMMITTEE OF EXPERTS ON ITS SIXTEENTH SESSION
(3-12 December 1990)

Addendum 6

Annex 7: Adopted text and amendments to chapters 15, 16 and 17 and Appendix of the Recommendations on the Transport of Dangerous Goods (Sixth revised edition) (ST/SG/AC.10/Rev.6).

Chapter 15

(a) In paragraph 15.1 change "table 15.1" to read "tables 15.1 and 15.2".

(b) In table 15.1 add two new entries to read:

Class	Packing Group	State	Maximum quantity per inner packaging
"5.2 c/	II	Solid	500 g
5.2 c/	II	Liquid	125 ml"

(c) Amend footnote (a) of table 15.1 to read:
"This limit may be increased to 1,000 ml for aerosols not containing toxic substance(s)".

(d) Amend footnote b/ to read:

"The organic peroxide should be of type B or C and should not require temperature control. See 11.3.3, 11.3.5 and footnote to 15.2 (e)."

(e) Insert a new footnote c/ to read:

"The organic peroxide should be of type D, E or F and should not require temperature control. See 11.3.3, 11.3.5 and footnote to 15.2 (e)."

(f) Change footnote c/ to read footnote d/ (twice - one in text (500 ml d/) and another in footnote).

(g) After table 15.1, add:

"Table 15.2: QUANTITY LIMITATIONS FOR CLASS 9

UN number	Proper shipping name	Maximum quantity per inner packaging
1941	DIBROMODIFLUOROMETHANE	5 l
2071	AMMONIUM NITRATE FERTILIZERS	5 kg
2209	FORMALDEHYDE SOLUTIONS	5 l "

Renumber 15.3 as 15.3.1 and add a new subparagraph 15.3.2.

"15.3.2. Shrink-wrapped or stretch-wrapped trays meeting the conditions of 9.3.1, 9.3.2 and 9.3.4 to 9.3.8 are acceptable as outer packagings for articles or inner packagings containing dangerous goods transported in accordance with these special recommendations. The total gross mass of the package should not exceed 20 kg."

Chapter 16

Where the word "metallic" occurs in relation to packagings, change to "metal".

(a) Insert a new subparagraph 16.1.6.8 to read:

"IBCs used for solids which may become liquid at temperatures likely to be encountered during transport should also be capable of containing the substance in the liquid state."

(b) 16.3.5.3, add the following note:

"Note. Average values should fall within these limits. Short-term fluctuations and measurement limitations may cause individual measurements to vary by up to ± 5% relative humidity without significant impairment of test reproducibility."

(c) Paragraph 16.4.9.5.4 (b) amend to read:

"For IBCs of types 31H1 and 31H2:- whichever is the greater of two values, the first as determined by one of the following methods:"
(i), (ii) and (iii) unchanged
"and the second as determined by the following method:"
(iv) unchanged

(d) Paragraph 16.5.5.1 insert after the first sentence:

"Another IBC of the same design may be used for the drop test as set out in paragraph 16.5.9.6"

(e) 16.5.8.4

Add following note:

"Note. Average values should fall within these limits. Short-term fluctuations and measurement limitations may cause individual measurements to vary by up to ± 5% relative humidity without significant impairment of test reproducibility."

(f) Paragraph 16.5.9.5.4 (b) amend to read:

"For IBCs of types 31HZ1 and 31HZ2:- whichever is the greater of two values, the first as determined by one of the following methods:"
(i), (ii) and (iii) unchanged
"and the second as determined by the following method:"
(iv) unchanged.

(g) 16.6.5.4

Add following note:

"Note. Average values should fall within these limits. Short-term fluctuations and measurement limitations may cause individual measurements to vary by up to ± 5% relative humidity without significant impairment of test reproducibility."

Chapter 17

(a) Amend paragraph 17.16 (a) and (b) to read as follows:

17.16 (a) for flammable gases, Division 2.1, 95%;

(b) for non-flammable, non-toxic gases, Division 2.2, 98%.

(b) Amend Table 17.1 to read as follows:

"TABLE 17.1 - List of Refrigerated Liquified Gases in Class 2 Transported in Tank-Containers

UN No.	Substance	Division	Subsidiary Risk Label	Special Requirements
1003	Air, refrigerated liquid	2.2	5.1	Lubricant for joints or other devices shall be inert to oxygen
1038	Ethylene, refrigerated liquid	2.1		
1073	Oxygen, refrigerated liquid	2.2	5.1	Lubricant for joints or other devices shall be inert to oxygen
1913	Neon, refrigerated liquid	2.2		
1951	Argon, refrigerated liquid	2.2		
1961	Ethane, refrigerated liquid	2.1		
1963	Helium, refrigerated liquid	2.2		

UN No.	Substance	Division	Subsidiary Risk Label	Special Requirements
1966	Hydrogen, refrigerated liquid	2.1		Carriage permitted under special conditions prescribed by the competent authorities. Frangible discs are allowed at the discretion of the competent authority.
1970	Krypton, refrigerated liquid	2.2		
1972	Methane, refrigerated liquid	2.1		
1972	Natural gas with a high methane content, refrigerated liquid	2.1		
1977	Nitrogen, refrigerated liquid	2.2		
2187	Carbon dioxide refrigerated liquid	2.2		
2201	Nitrous oxide, refrigerated liquid	2.2		Lubricants for joints or other devices shall be inert to oxygen
2591	Xenon, refrigerated liquid	2.2		
3138	Ethylene, acetylene and propylene in mixtures, refrigerated liquid; containing at least 71.5% ethylene with not more than 22.5% acetylene and not more than 6% propylene	2.1		

APPENDIX

List of Generic or N.O.S. Proper Shipping Names

The following list contains the main generic entries and all the N.O.S. entries given in chapter 2. When a substance is not listed by name in chapter 2, this list may be used as an aid to finding the most appropriate generic or N.O.S. Proper Shipping Name. The most specific applicable name should always be used.

Names are shown grouped under each Class and Division. Within each Class or Division the more specific names are listed first.

Class or Division	Subsidiary Risk	UN Number	Proper Shipping Name

(TABLE TO BE CONSTRUCTED)